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SORPTION BEHAVIOR OF ORGANIC PYROPOLYMERS IN AQUEOUS SOLUTION

by

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Summary

The sorption behavior of the pyrolysis products (pyropolymers) of organic polymers was investigated. The results indicate that the pyropolymers of poly (vinyl chloride) exhibit selective adsorption towards the herbicide 2-sec-butyl-4,6-dinitrophenol but none to 2,4-dichlorophenoxyacetic acid. The initial rate of adsorption during the first hour is almost twice that of activated carbon with a total uptake of approximately 30% depending on the preparative conditions of the pyropolymers. However, unlike activated carbon, the pyropolymers of poly (vinyl chloride) slowly releases the adsorbate. This release is probably due to the displacement of the adsorbate by water molecules. While the initial adsorption followed by release is unusual, this property of the pyropolymer might find useful applications. The capability of the pyropolymers of poly (vinyl chloride) to adsorb the herbicide is greatly influenced by the preparative conditions. No adsorption was observed with the pyrolytic conversion products of poly [N,N'-(p,p'-oxydiphenylene) pyromellitimide] ("Kapton"). The lack of adsorption is probably due to the fact that the starting material is commercially available only in the form of smooth film with no porosity rather than due to its chemical structure. Considerable further work is needed to elucidate the structure of the pyropolymers, to define the exact preparative conditions and to measure the surface areas.

I. Introduction

Water renovation demands the efficient removal of soluble refractory organic materials and ions from secondary effluents. This process may be carried out with activated carbon granules, the adsorption properties of which have been the subject of investigations by Morris and Weber (1, 2). Despite its high effectiveness, activated carbon is relatively expensive and some problems are encountered in the regeneration process.

The object of this preliminary feasibility study was to evaluate the sorption properties of selected organic pyropolymers especially with respect to organic materials and to compare the results with those obtained with activated carbons by other workers.

II. Background

The thermal degradation of polymers follows largely free-radical initiated chain reactions. During the degradation two processes can take place; chain scission and/or crosslinking. Polymers in which the "backbone" undergoes mainly scission usually vaporize completely without leaving any appreciable quantity of residue when heated (pyrolyzed) for prolonged periods. This is not the case with polymers in which the formation of crosslinks occurs. These materials become stablized due to the formation of a rigid insoluble network; the stable products are referred to as pyropolymers.

Unlike activated carbons, many pyropolymers are characterized by the presence of a large number of hetero atoms having excess electrons and/or

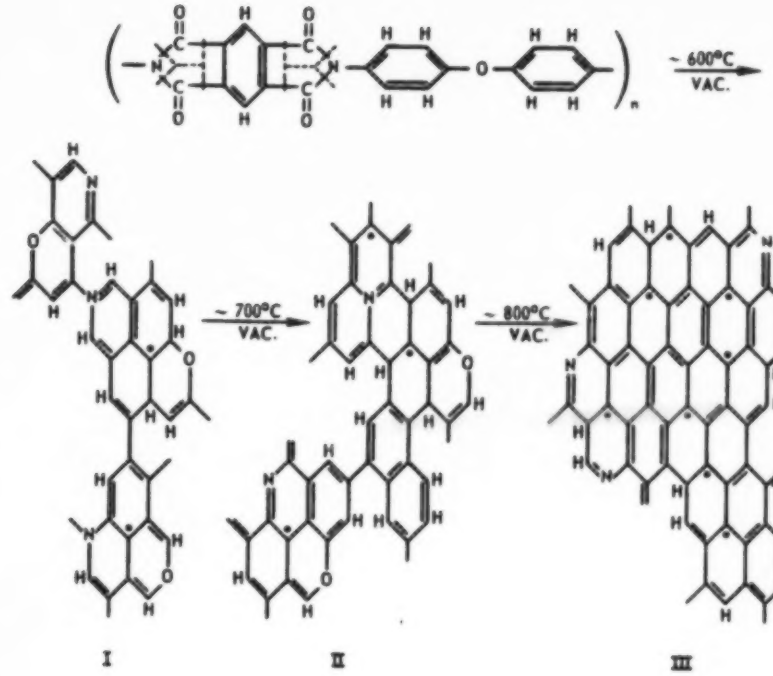
unsaturated bonds. This property and the possibility that the microporosity of the pyropolymers might be altered by varying the preparative conditions, make these systems interesting candidates for the study of sorption-desorption cycles and for the elucidation of the physico-chemical parameters that enhance these processes. By understanding these phenomena it should be possible to "design" additional substrates for the removal of specific organic materials and/or inorganic ions from waste water.

III. Approach

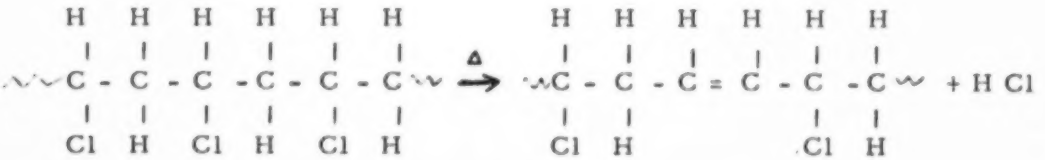
The herbicides 2-sec-butyl-4,6-dinitrophenol and 2,4-dichlorophenoxyacetic acid were selected as adsorbates. These materials are among the typical organic pollutants in waste water. Furthermore, considerable previous work has been done by other workers with these herbicides using activated carbon as the adsorbent (1,2).

The pyropolymers were prepared from (1) poly (vinyl chloride), obtained from the Dow Chemical Company, and (2) poly [N,N'-(p,p'-oxydiphenylene) pyromellitimide], commercially available from duPont as "Kapton" or "H"-film.

Upon thermal degradation, both of these polymers leave a residue (pyropolymer) depending on the temperature and time of the pyrolysis. The mechanism of thermal degradation of the polyimide has been extensively studied by Bruck (3-9) and involves the cleavage of the imide groups with the elimination of carbon monoxide and the subsequent formation of a condensed polynuclear system. The following scheme has been postulated by Bruck (4):



The thermal degradation of poly (vinyl chloride) involves the abstraction of a hydrogen atom from an adjacent carbon and formation of a double bond (10):



With further pyrolysis the double-bonded chains cluster into aromatic rings forming a network structure.

IV. Experimental Details

(A) Preparation of the Adsorbent

1. Vacuum Pyrolysis

Vacuum pyrolysis was used only in the case of poly [N, N'-(p, p'-oxydiphenylene) pyromellitimide]. This material is commercially available only as a film. An accurately weighed two-mil (0.002 inch) thickness sample of the polymer film was placed in a pyrex glass tube which was connected to a conventional high vacuum system. The system was evacuated to approximately 2×10^{-5} mm of Hg, then the preheated furnace was raised into position around the sample tube and the polymer pyrolyzed for predetermined periods.

2. Pyrolysis in Oxygen and/or Nitrogen

Poly (vinyl chloride) was pyrolyzed in a gaseous atmosphere in the presence of nitrogen. The pyrolyzed polymer was pulverized to a size of 40/60, that is, particles which pass through a U.S. Standard Sieve No. 40 but not through a No. 60.

Poly [N, N'-(p, p'-oxydiphenylene) pyromellitimide] was first pyrolyzed in oxygen (353 ml/min) at 450°C for two hours followed by pyrolysis in nitrogen (283 ml/min) at 450°C for an additional 30 minutes to a total weight loss of 32.4%.

(B) Adsorption Experiments

The adsorption studies were carried out by a simple stirred-batch-reactor technique at room temperature ($25^{\circ} \pm 2^{\circ}$C). An aqueous solution (1000 ml.) of the herbicide was prepared with ion-exchange treated water. The solution was

filtered into a one-liter pyrex round bottom glass bottle and was allowed to reach the desired temperature and adsorptive equilibrium with the surface of the glass bottle. Prior to the introduction of the accurately weighed adsorbent, an initial sample was removed and its concentration determined spectrophotometrically. The adsorbent was then introduced into the aqueous solution and rapidly dispersed with a "Teflon"-coated magnetic stirrer. At predetermined intervals the stirring was interrupted and the adsorbent particles allowed to settle. Approximately three milliliters of the clear supernatant liquid were pipetted out for analysis. Although this resulted in a slight diminuition of the solution, the estimated cumulative error was not considered significant enough to materially influence the results in this preliminary feasibility study.

(C) Spectrophotometry

Two spectrophotometers were used in this work: a Zeiss PMQ II single beam instrument and a Bausch and Lomb Spectronic 505 double beam instrument. Figure 1 shows the ultraviolet absorption spectrum of 2-sec-butyl-4,6-dinitrophenol. The calibration curve is shown by Figure 2.

V. Results and Discussion

Of the two classes of pyropolymers investigated only samples prepared from poly (vinyl chloride) showed adsorption properties. Furthermore, a selective adsorption process was observed, inasmuch as the herbicide 2-sec-butyl-4,6-dinitrophenol was taken up preferentially over the herbicide 2,4-dichlorophenoxyacetic acid. The pyropolymers were prepared in a nitrogen atmosphere (535 ml/min.) and pyrolyzed for 30 minutes between 250^{o} and

ABSORPTION SPECTRUM FOR 2-SEC-BUTYL-4, 6-DINITROPHENOL;
CELL LENGTH 1 CM, CONCENTRATION = 52.5 μMOL/LITER

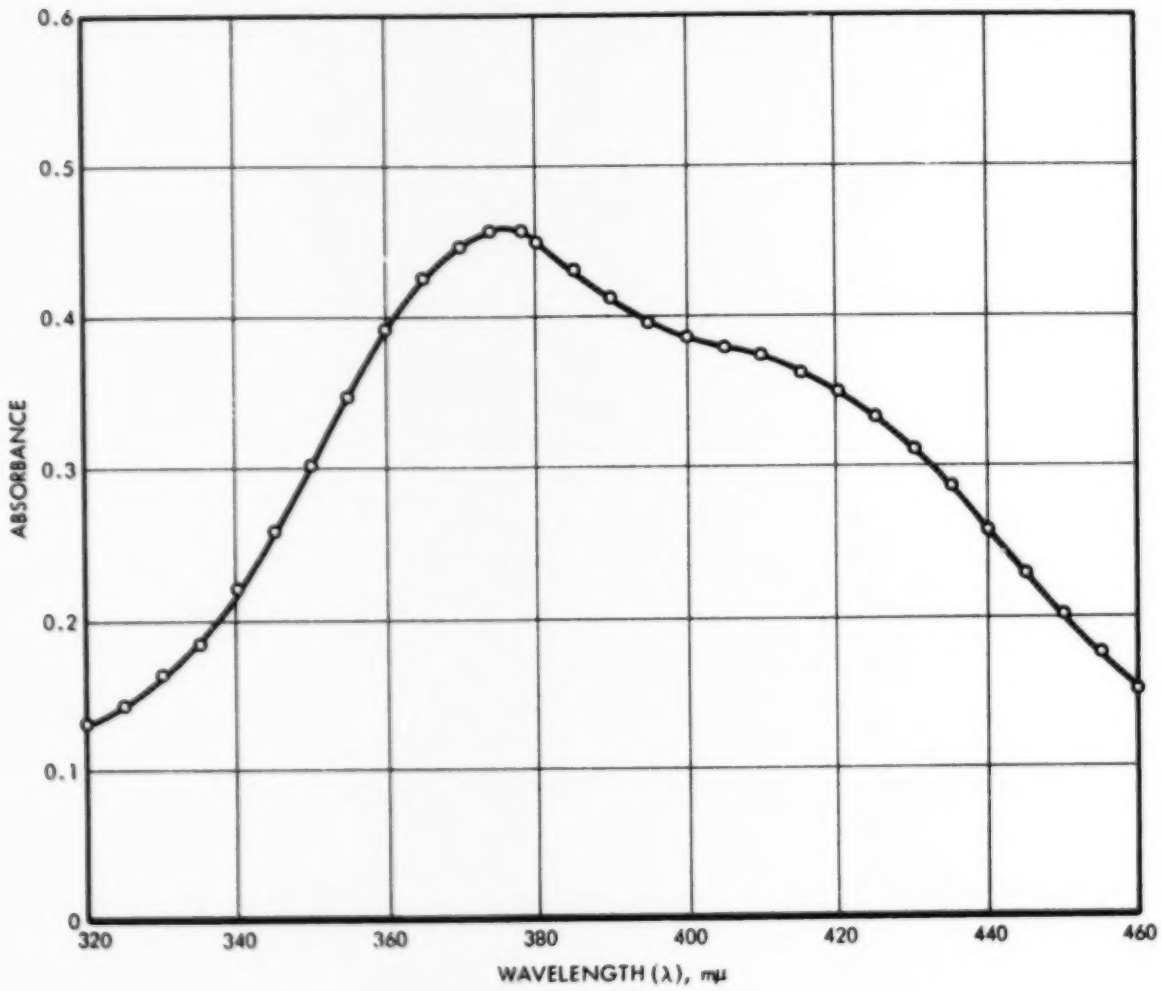


FIGURE 1

CALIBRATION CURVE FOR 2-SEC-BUTYL-4, 6-DINITROPHENOL;
CELL LENGTH 1 CM, WAVELENGTH = 375 mμ

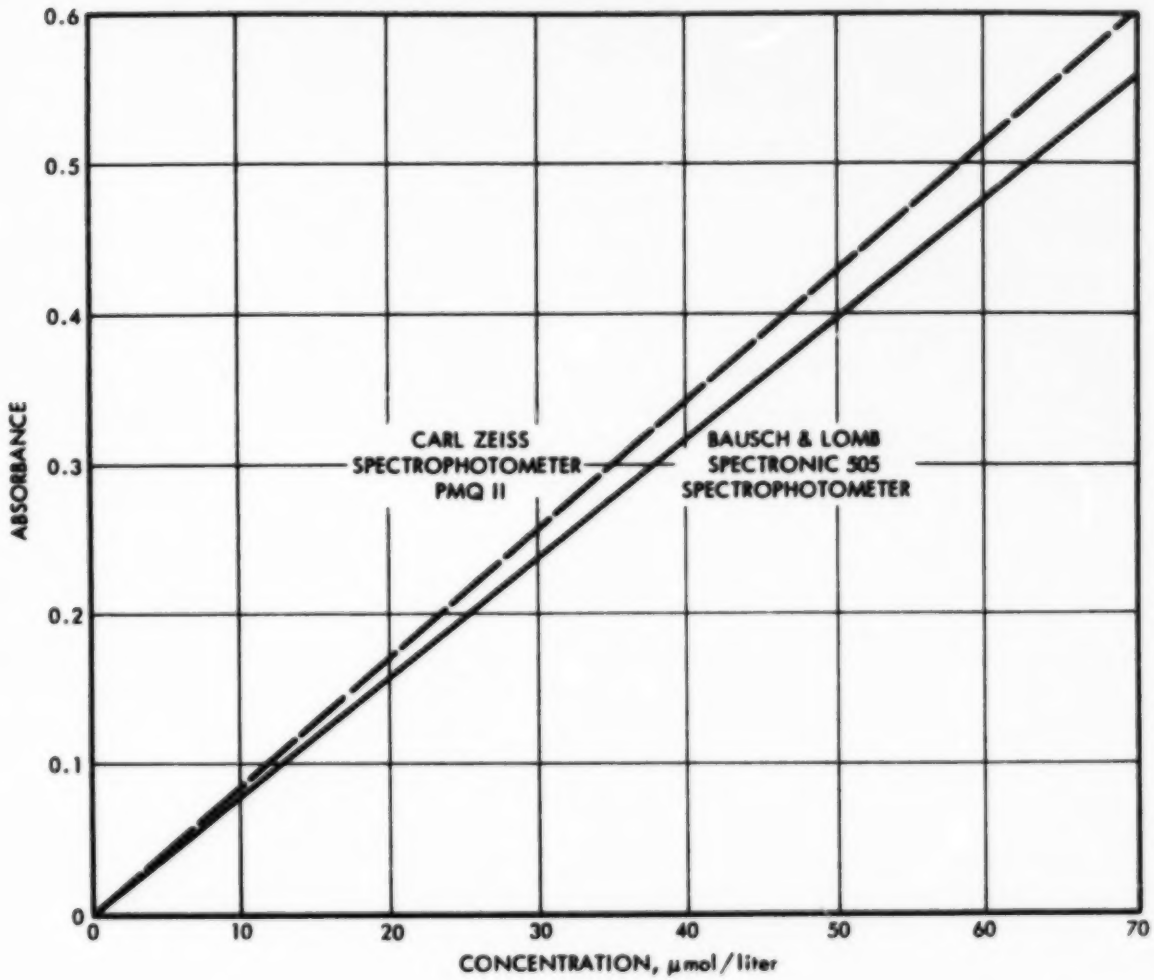


FIGURE 2

275°C. The adsorption properties of these pyropolymers were very significantly influenced by the extent of volatilization (weight loss) as shown in Table 1.

Table 1

Adsorptive Capacity of Pyropolymers (Size 40/60) of Poly (vinyl chloride) with Extent of Volatilization Using 2-sec-butyl-4,6-dinitrophenol

Volatilization, %	Adsorption
14.3	none
18.2	8% max. in 5 hr; initial conc. 46 micro mol/lit.
27.4	30% max. in 1 hr; initial conc. 71 micro mol/lit.
28.4	30% max. in 1 hr; initial conc. 71 micro mol/lit.
33.3	none
45.0	none
50.0	none
Columbia Activated Carbon (Size 20/48)	8% max. in 1 hr; initial conc. 60 micro mol/lit.

With an aqueous solution of 2-sec-butyl-4,6-dinitrophenol having an initial concentration of 71 micro mol/liter, approximately 30% of the herbicide was taken up during the first hour by samples of the pyropolymers which had been heat-treated to a weight loss of 27 to 28%. On the other hand, only 8% herbicide uptake was shown with another sample of the pyropolymer which had been pyrolyzed to a weight loss of 18.2%. No adsorption was observed with the other samples. Furthermore, the pyropolymers adsorbed only the herbicide 2-sec-butyl-4,6-dinitrophenol and not 2,4-dichlorophenoxyacetic acid. This selective adsorptive capactiy of the pyropolymers is unusual inasmuch as activated carbon does not show such property (1,2). This great dependence of the adsorptive power of the

pyropolymers on the extent of weight loss is most likely associated with the formation of a network structure with various degrees of "tightness," the presence of hetero atoms (Cl) and the surface areas.

Figure 3 shows the adsorption curve for 2-sec-butyl-4,6-dinitrophenol with the pyropolymers of poly (vinyl chloride) which had been thermally degraded to a weight loss of 27.4%. An initial rapid decrease is observed in the concentration of the herbicide during the first hour. Then a gradual increase in the concentration follows. The total initial adsorption is approximately 30% and almost twice the initial rate of adsorption shown by Columbia activated carbon (particle size 20/48). A much smaller initial adsorption was observed with the pyropolymer of poly (vinyl chloride) that had been pyrolyzed to a weight loss of 18.2% as seen in Figures 4 and 5. The total adsorption after the first five hours was approximately 8%, followed by a gradual release of the herbicide.

Figures 6 and 7 illustrate the adsorption and rate curves, respectively, for the activated carbon. Unlike the pyropolymers, activated carbon retains the adsorbent. The release of the herbicide by the pyropolymer after its initial adsorption might be due to a gradual displacement by water of the herbicide from the surface of the adsorbent.

The results underline the importance of the preparative conditions for the pyropolymers. Since very little information is known about the structre of these systems, much further work is needed (including surface area measurements) to elucidate more clearly the parameters involved in the adsorption process.

ADSORPTION CURVE FOR 2-SEC-BUTYL-4, 6-DINITROPHENOL
WITH 27.4% WEIGHT LOSS PYROLYSIS PRODUCT OF PVC

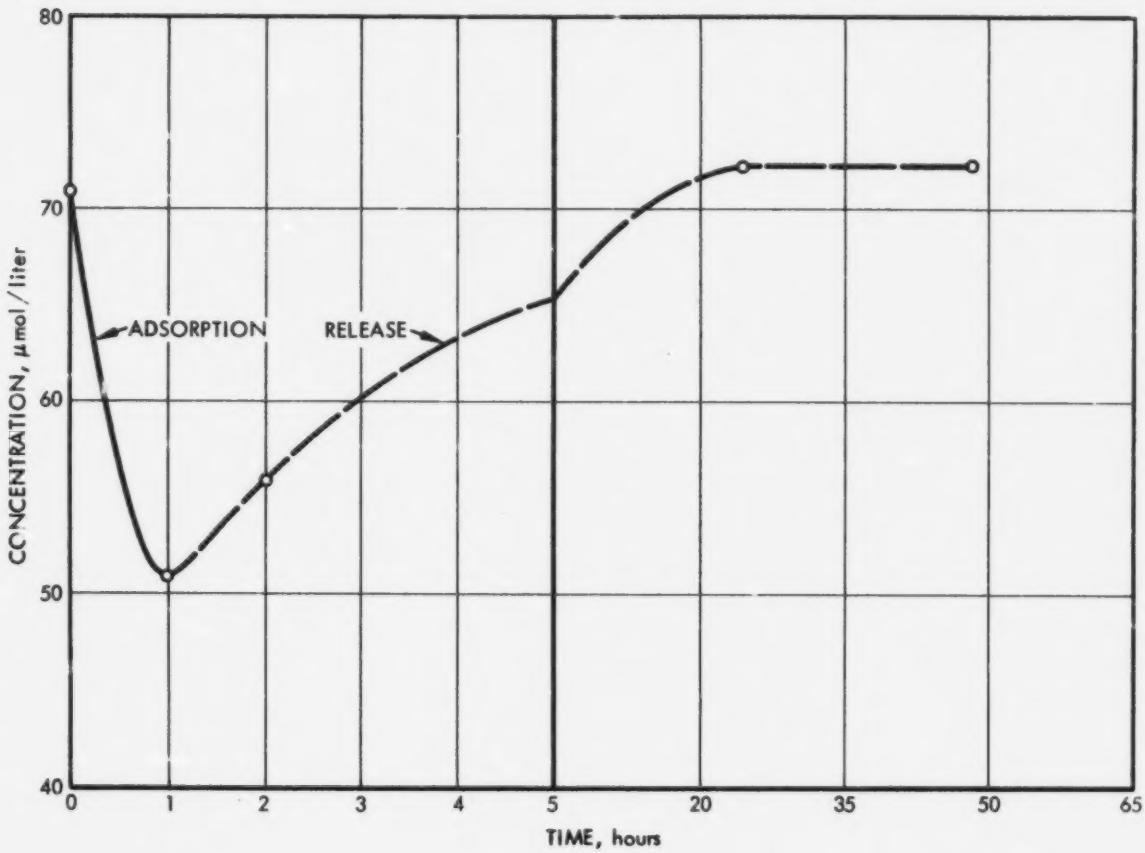


FIGURE 3

ADSORPTION CURVE FOR 2-SEC-BUTYL-4, 6-DINITROPHENOL
WITH 18.2% WEIGHT LOSS PYROLYSIS PRODUCT OF PVC

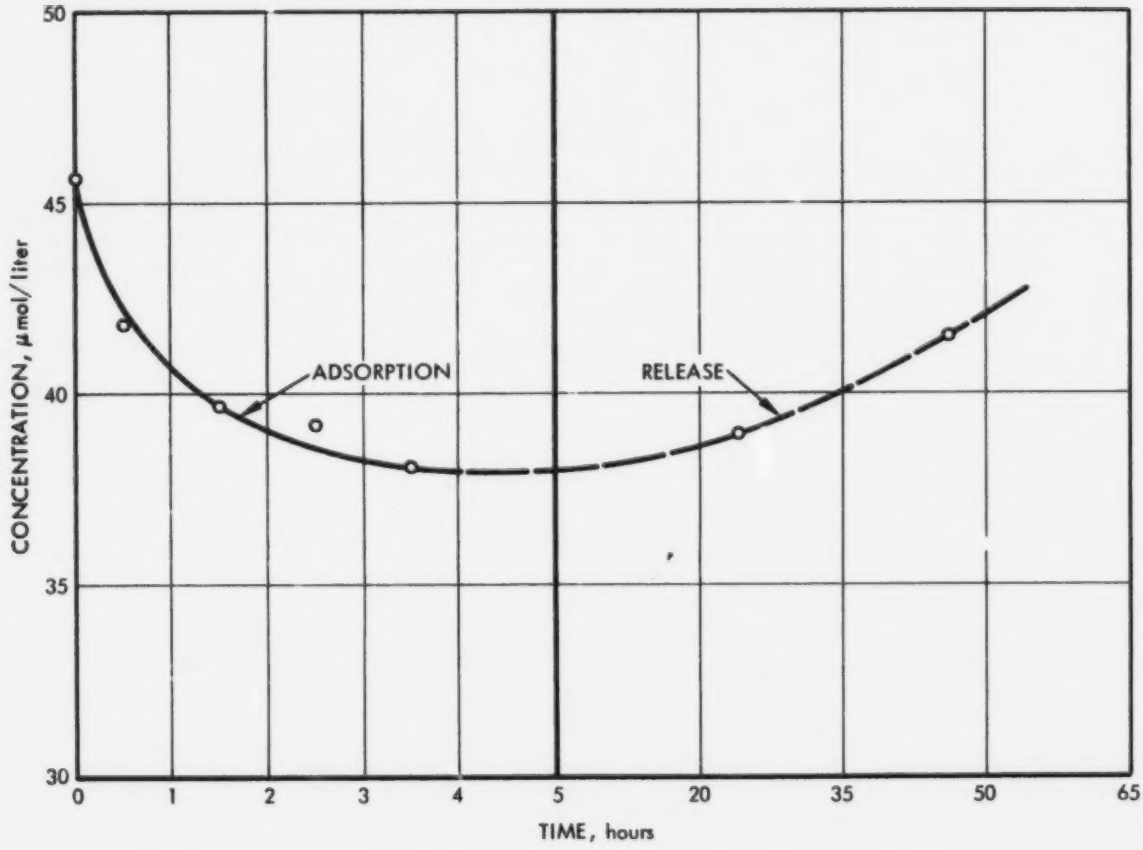


FIGURE 4

RATE OF ADSORPTION OF 2-SEC-BUTYL-4, 6-DINITROPHENOL
ON 18.2% WEIGHT LOSS PYROLYSIS PRODUCT OF PVC

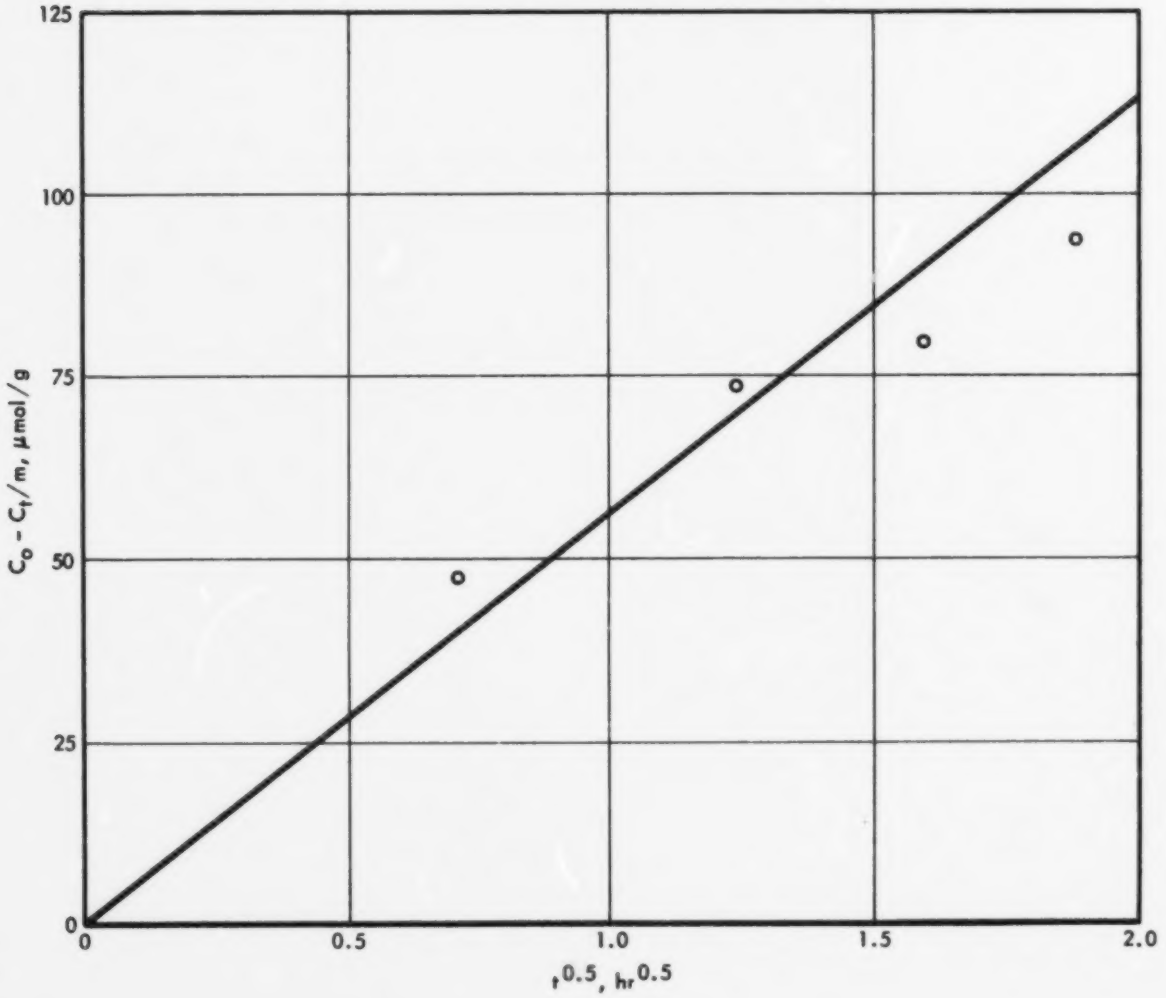


FIGURE 5

ADSORPTION CURVE FOR 2-SEC-BUTYL-4, 6-DINITROPHENOL
WITH COLUMBIA ACTIVATED CARBON

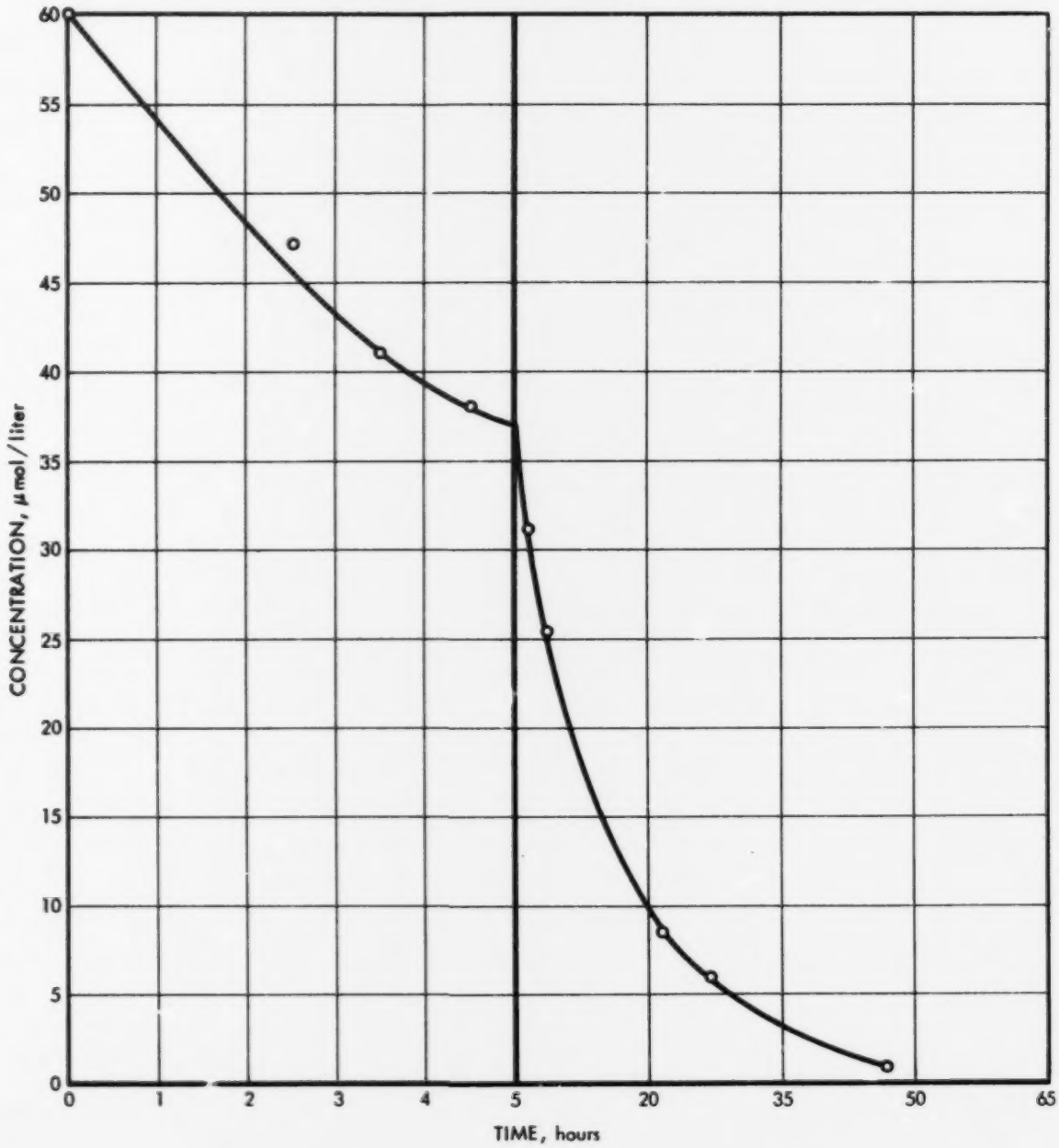


FIGURE 6

RATE OF ADSORPTION OF 2-SEC-BUTYL-4, 6-DINITROPHENOL
ON COLUMBIA ACTIVATED CARBON

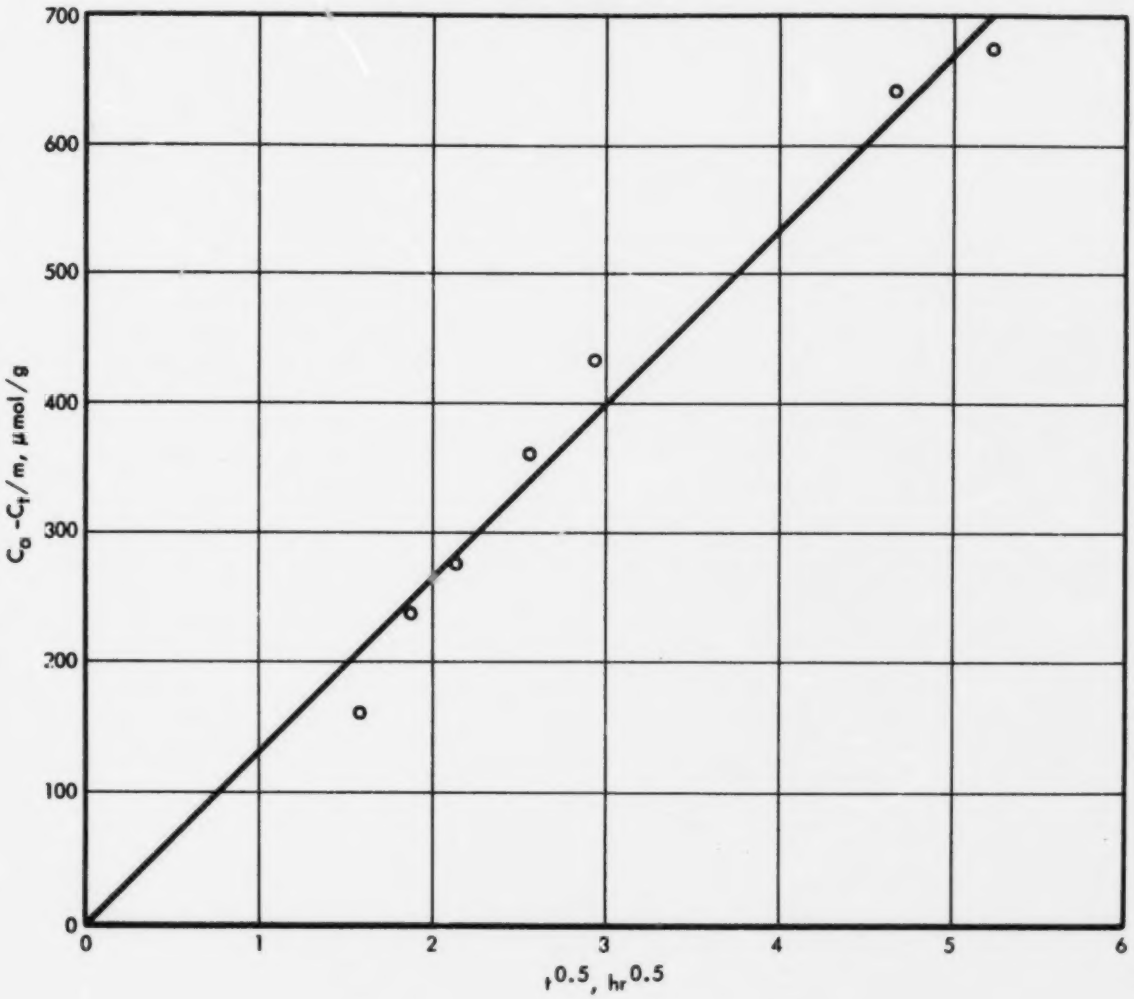


FIGURE 7

The pyropolymers prepared from poly [N, N'-(p, p'-oxydiphenylene) pyromellitimide] films ("Kapton" or "H"-film) showed no adsorptive properties toward either of the two herbicides. The pyropolymers were prepared in a vacuum and also in an oxygen/nitrogen atmosphere. The vacuum pyrolysis was carried out at 600°C (2×10^{-5} mm of Hg) for two hours to a total weight loss of 39%. The gaseous pyrolysis was first carried out in oxygen (353 ml/min.) at 450°C for two hours followed by further heat-treatment in nitrogen (283 ml/min.) at 450°C for 30 minutes to a total weight loss of 32.4%. The lack of adsorptive capacity of this pyropolymer is probably due not so much to its chemical structure but rather to a lack of porosity of the material (film). Present commercial preparative conditions require a two-step process which involves a diffusion controlled cyclization reaction after the precursor polyamic acide is cast as a film. The very smooth, with no apparent porosity, surface of this film is retained even after pyrolysis. Hence the lack of adsorption is likely to be associated with the surface properties of this polymer.

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